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Langley

(54) METHOD FOR THE INTEGRATION OF CARBOCHLORINATION INTO A STAGED REFORMING OPERATION AS AN ALTERNATIVE TO DIRECT RESIDUE OXIDATION FOR THE RECOVERY OF VALUABLE METALS

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(56) References Cited

U.S. PATENT DOCUMENTS

(10) Patent No.: US 9,163,297 B2 (45) Date of Patent: Oct. 20, 2015

4,045,461 A * 8/1977 Kiovsky et al. 518/718 (Continued)

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS

"Commercial and Industrial Practices for Activated Carbon Management" from Disposal of Activated Carbon from Chemical Agent Disposal Facilities. National Research Council of the National Academies, p. 46. 2009.*

(Continued)

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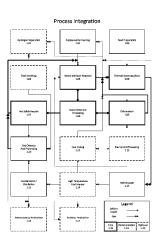
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(57) ABSTRACT

Method of combining industrial processes having inherent carbon capture and conversion capabilities offering maximum flexibility, efficiency, and economics while enabling environmentally and sustainably sound practices. Maximum chemical energy is retained throughout feedstock processing. A hybrid thermochemical cycle couples staged reforming with hydrogen production and chlorination. Hydrogen generated is used to upgrade feedstocks including bitumen, shale, coal, and biomass. Residues of upgrading are chlorinated, metals of interest are removed, and the remainder is reacted with ammonia solution and carbon dioxide to form carbonate minerals. The combination provides emissions free production of synthetic crude oil and derivatives, as well as various metals and fertilizers. Sand and carbonate minerals are potentially the only waste streams. Through this novel processing, major carbon dioxide reduction is afforded byminimizing direct oxidation. Supplemental heat to run the reactions is obtained through external means such as concentrated solar, geothermal, or nuclear.

39 Claims, 1 Drawing Sheet



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(56)	Refe	erences Cited		

5 (2013.01); <i>102W</i>	Synthesis, freat and I ower integra
30/54 (2015 05)	Biomass Coal and Natural Gas

U.S. PATENT DOCUMENTS

4,243,639	A *	1/1981	Haas et al 423/63
4,664,849	A	5/1987	Farrington et al.
4,786,319	A	11/1988	Zeiringer
5,039,336	A	8/1991	Feuling
5,569,440	A	10/1996	Sommers
6,558,454	B1*	5/2003	Chang et al 95/901
7.674.443	B1	3/2010	Davis

2007/0224109	A1*	9/2007	Chaifetz et al 423/491
2008/0256952	A1*	10/2008	Litwin et al 60/641.8
2010/0113624	A1	5/2010	Routier
2011/0262323	A1*	10/2011	Rappas et al 423/63
2012/0031232	A1	2/2012	Huang
2012/0073198	A1	3/2012	Goel et al.
2013/0005838	A1*	1/2013	Eilos et al 518/703
2013/0020538	A1	1/2013	Bingham
2013/0039824	A1	2/2013	Abu-Sharkh

OTHER PUBLICATIONS

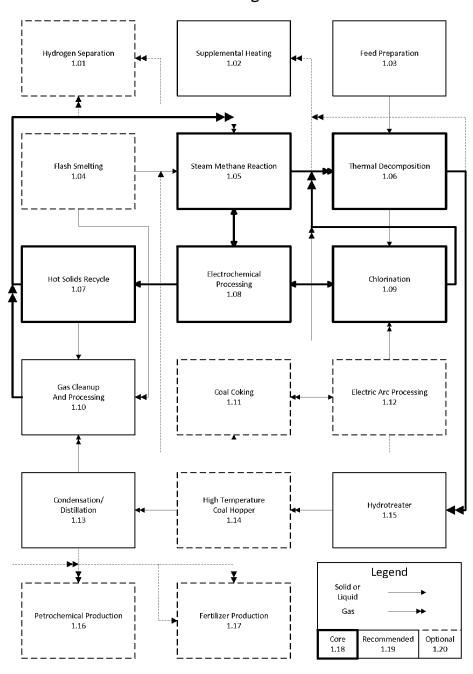
Baliban et al., Optimization Framework for the Simultaneous Process Synthesis, Heat and Power Integration of a Thermochemical Hybrid Biomass, Coal, and Natural Gas Facility, Computers & Chemical Engineering, Sep. 2011, pp. 1647-1690, vol. 35, Issue 9, Elsevier. Cai et al., Development of Multifunctional Energy Systems, Energy, Nov. 2010, pp. 4375-4382, vol. 35, Issue 11, Elsevier. International Search Report for International Application No. PCT/

US2013/053980, mailed Feb. 7, 2014,8 pages, U.S. International Search Authority, Alexandria, Virginia.

Martynov et al., Water and Hydrogen in Heavy Liquid Metal Coolant Technology, Progress in Nuclear Technology (2005) pp. 604-615, vol. 47, Issues 1-4, Elsevier, Great Britain.

^{*} cited by examiner

Figure 1
Process Integration



METHOD FOR THE INTEGRATION OF CARBOCHLORINATION INTO A STAGED REFORMING OPERATION AS AN ALTERNATIVE TO DIRECT RESIDUE OXIDATION FOR THE RECOVERY OF VALUABLE METALS

RELATED APPLICATIONS

This application claims priority to the provisional U.S. ¹⁰ Application No. 61680393, filed on Aug. 7 2012.

This application claims priority to the provisional U.S. Application No. 61786477, filed on Mar. 15 2013.

TECHNICAL FIELD

The present invention relates generally to a system and method for improved material utilization in industrial processing. More specifically, the present invention addresses existing challenges with carbon and waste stream management of major processes of the petrochemical and metallurgy industries. More specifically still, the present invention utilizes a reconfigurable set of processes hot-coupled to each other enabling high-efficiency carbon capture and conversion as well as comprehensive waste stream management capabilities ideal for new plant design or retrofit.

BACKGROUND ART

Rising demand for fossil fuels, exasperated by rapidly 30 developing nations, is driving the need for more efficient utilization of limited natural resources in conjunction with the development of alternative energy sources. Many modern advances in long utilized petrochemical practices such as gasification and hydrotreatment are enabling the cost effec- 35 tive utilization of so called unconventional fuels. Hybrid designs such as those discussed in papers "Development of Multifunctional Energy Systems" (Cai et al., Energy, 2010) and "Optimization Framework for the Simultaneous Process Synthesis, Heat and Power Integration of a Thermochemical 40 Hybrid Biomass, Coal, and Natural Gas Facility" (Baliban et al., Computers & Chemical Engineering, 2011) enable the conversion of non-conventional fuels such as coal and natural gas as well as biomass and waste to be converted to direct replacements or additives for petrochemicals conventionally 45 derived from oil. Furthermore, they are capable of utilizing carbon dioxide as a carbon source for conversion to synthetic fuels, oils, and other carbon materials.

These practices do have substantial costs involved however. Capitol costs of equipment as well as further energy 50 costs are incurred depending on the chosen technology and level of carbon dioxide management sought. The reliance on air separation techniques common in high efficiency and especially carbon sequestration applications is one substantial cost. Further notable costs of such systems are hydrogen 55 production methods that typically rely on direct oxidation of fuel inputs which in turn puts a greater load on carbon capture systems. An alternative method of hydrogen production via electrolysis is emissions free but even with onsite electricity production (which typically is not emissions free or highly 60 efficient) represents a steep energy penalty. Even state of the art staged reforming processes coupled to numerous complementary subsystems rely to a large extent on legacy practices of energy production through direct oxidation and may or may not manage the resulting carbon dioxide produced. (US 65 2012/0073198 A1, U.S. Pat. No. 7,674,443) What is needed is a superstructure that takes advantage of the level of maturity

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of such legacy processes while integrating advances in alternative energy sources to efficiently deliver process heat. The present invention accomplishes this through the novel integration of hydrogen production with the indirect oxidation by carbochlorination of pyrolysis residues. Through this arrangement, heat is conserved and directed at hydrogen production and carbon dioxide formation is kept to a minimum.

Martynov et al. has shown in "Water and Hydrogen in Heavy Liquid Metal Coolant Technology" (Progress in Nuclear Technology, 2005) that molten lead-bismuth eutectic is an ideal catalyst for steam methane reactions. Combining this advantageous method of hydrogen production with heat amplification techniques allows for a range of viable alternative energy inputs such as direct or indirect heating provided by an advanced high temperature modular nuclear reactor.

Through this unique arrangement of processes, a large number of metallurgical subsystems may be integrated with a variety of synergistic benefits. Those of ordinary skill in the art should recognize the integration of a flash smelter provides for both the management of smelter off gases and an inherent drossing mechanism within the molten metal steam methane reactor. Similarly, steel production through recycling and direct reduction can be incorporated with highly beneficial off gas processing simultaneously complementing the carbochlorination process. A variety of processing methods are available for the extraction of valuable base metals from the feedstock through gaseous and electrochemical methods. In addition to the precious metals inherently captured by the molten metal steam methane reforming, rare earth elements (as well as the various radioactive species typically associated with them) are captured and concentrated by carbochlorination techniques that can be removed through methods already known in the art. (U.S. Pat. Nos. 5,039,336, 5,569,440) Also disclosed is a method of oxidizing the carbon component of carbochlorination residue using metal oxides from integrated processes as well as a novel electrochemical cationic exchange for extraction of residual components utilizing a solid electrolyte. (U.S. Pat. No. 4,664,849) Those of ordinary skill in the art will undoubtedly recognize other varying benefits of the process integration enabled by the present invention.

Finally, by exploiting a staged reforming operation utilizing hydrogen produced in the steam methane reactor, oxidation of feedstock is minimized and hydrogenation is maximized. Feedstock impurities are internally managed and a plurality of options for their removal is available. One of the more unique features enabled is the production of carbonate minerals through a modified Solvay process utilizing the metal chlorides produced via carbochlorination. (EP 0013586 B1, US 2013/0039824 A1) This along with internal reprocessing of carbon dioxide relieves or eliminates the need for dedicated carbon capture subsystems and their attributed energy losses.

DISCLOSURE OF INVENTION

The present invention addresses the issue of carbon dioxide management in a staged reforming operation through tightly integrating methods of petrochemical processing, metallurgy, and ammonia-soda processing. Heat is generated by methods external to the invention and used to raise feedstock temperature to a predetermined level. Heat amplification as well as emissions management is inherently embodied within the invention by multiple direct contact heat exchanges between integrated processes. Thermal energy accumulated in the high-temperature subsystems is dissipated through endothermic steam methane reactions producing bulk hydrogen for

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consumption by coupled processes. Within these high temperature subsystems, heat from the carbochlorination of pyrolysis residues is generated and supplemented through the hot-coupling of further integrated processes. Carbon dioxide generated in carbochlorination is stripped of metal chlorides and combined with produced hydrogen to form a synthesis gas. This hot synthesis gas is employed in the pyrolysis of the feedstock and the combined gases are sent to a hydrotreatment vessel for upgrading and removal of impurities such as sulfur, halogens, nitrogen, and heavy metals. Gaseous impurities such as hydrogen chloride and hydrogen sulfide are removed from the gas stream following condensation of the higher molecular weight hydrocarbons and the remaining gases are further processed or recycled through the system. Base metals can be extracted as gaseous or liquid chlorides, separated and processed to oxides or another separable form, or removed through electro-deposition. Noble metals are removed with lead, copper, and related metals as dross from the steam methane reactor. Rare earth and radioactive elements present are concentrated by the carbochlorination and 20 removed through cationic exchange, leaching, electrochemical, or other means. The remaining metal chlorides consisting substantially of alkali/alkaline chlorides as well as metal oxides consisting substantially of silica with varying amounts mixed oxide minerals transfer their useful heat to the input 25 follows: streams and the chlorides may be utilized in a modified Solvay process producing ammonium chloride and carbonate minerals. Carbon dioxide not mineralized is further processed through a reverse water gas shift reactor or other dedicated processing equipment as part of the gas cleanup and $\ ^{30}$ processing or recycled through the system. Carbon management is thus handled through minimization of direct oxidation, mineralization, and synthesis gas reprocessing.

BRIEF DESCRIPTION OF DRAWINGS

Further features, advantages and characteristics of the present invention will become apparent to a person of ordinary skill in the art from the following detailed description of best modes of carrying out the present invention, made with 40 reference to the included drawing, in which the reference numbers used for selected subsystems are listed in order of appearance rather than by importance or stepwise fashion, and in which:

FIG. 1 illustrates the process integration of a number of 45 embodiments of the present invention. Subsystems in bold are considered to be integral to the operation. Solid lighter outlined subsystems are believed to be ideal to the operation, however alternatives are known to exist and there may be advantageous arrangements not accounted for in the illustra- 50 tion. Dashed subsystems are considered to be advantageous embodiments but their exclusion is not considered detrimental in any way. Double arrowed lines represent gas streams and single arrows represent solids or (usually high temperature) liquids.

BEST MODES FOR CARRYING OUT THE INVENTION

With reference to FIG. 1, multiple configurations of the 60 present invention can be arranged through the inclusion, exclusion, or modification of various subsystems. To those of ordinary skill in the art it should become apparent that only a subset of applicable subsystems has been included in the drawing and this should in no way limit the present invention 65 to such subset. In accordance with a best mode of carrying out the present invention the drawing illustrates the integration of

staged reforming with residue chlorination featuring inherent carbon oxide, heat, and waste management.

In accordance with best modes, all examples are implied to have attached to them an advanced high temperature nuclear reactor as a zero emissions heat source. Furthermore, all supplementary heating, cooling, and electricity required by the combination of integrated processes in the examples is assumed to be provided by said reactor and related apparatus. For the purpose of this disclosure, supplementary should be defined as any energy requirements not met by thermochemical changes within the proposed set of integrated subsystems. Further, in the examples it should be assumed that an outlet temperature of roughly 700 degrees centigrade is provided by the Supplemental Heating (1.02) and the heating costs of said arrangement are on par with coal. All of the Core components: Steam Methane Reaction (1.05), Thermal Decomposition (1.06), Hot Solids Recycle (1.07), Electrochemical Processing (1.08), and Chlorination (1.09) plus all of the Recommended components: Supplemental Heating (1.02), Feed Preparation (1.03), Gas Cleanup and Processing (1.10), Condensation/Distillation (1.13), and Hydrotreatment (1.15) are assumed to be included in the examples.

For the purpose of further reference within the examples a brief explanation of the subsystems shown in FIG. 1 is as

- 1.01 Hydrogen Separation is to include any number of known technologies for the production or separation of purified hydrogen for use or sale. The bulk hydrogen production will be assumed to proceed via the Steam Methane Reaction (1.05) subsystem and the current subsystem is to supplement the bulk hydrogen production through methods including purification by molecular sieves, pressure swing absorption, proton conducting ceramics, but is also meant to include production techniques such as electrolysis.
- 1.02 Supplemental Heating is to include heat generated or used outside of and supplemental to other integrated subsystems. This may include a conventional boiler, gas or combined cycle turbine, or fuel cell; in which case it converts produced gas into electricity for sale or use. This subsystem is also meant to include any means of external energy input such as direct or indirect heating or heat recovery as well as electricity from solar, wind, or hydro for example. In most cases it is assumed that this supplemental energy is input substantially through steam to the Steam Methane Reaction (1.05) or through electricity for the Electrochemical Processing (1.08). Combined cycle configurations such as waste heat capture through desalination would also be included in this subsystem.
- 1.03 Feed Preparation is to include any crushing, grinding, blending, pulping, pelletizing, de-watering, pre-heating or related pre-processing applied to the feedstock which may be located on premise or at a remote facility. The overall pre-processing required is assumed to be largely dependent on locally available resources and in turn impact the applicability of the integration of various subsystems within a given locale. Essentially any materials may be prepared and decomposed by the overall processing with the only limitations to feedstock being whether it economically meets the design requirements through local availability constraints.
- 1.04 Flash Smelting is to include the necessary apparatus for the smelting of sulfide ores or more precisely ore concentrates. This is to include both primary and secondary smelting. In conjunction with conventional flash smelting this is to include means of oxidizing molten

lead from the Steam Methane Reaction (1.05) and its utilization within this subsystem or other applicable subsystems. Preferably this means of oxidation provides a heated stream of nitrogen enriched air to be utilized in other subsystems. All outputs from this subsystem are 5 preferably sent advantageously to other subsystems; lead bullion to the Steam Methane Reaction (1.05), slag to Chlorination (1.09), and sulfur dioxide to a Claus plant in Gas Cleanup and Processing (1.10) for example. A further noteworthy use of this subsystem may be 10 expanded to calcination without exceeding its disclosed scope.

- 1.05 Steam Methane Reaction is to include any configuration of a reactor or reactors operating by reacting steam with molten lead or lead alloy at moderate to high temperature. Further included are means or methods of removing oxygen from the molten lead or lead alloy such as reaction with methane or other gases, use of a solid oxide conducting ceramic, or direct carbon reduction for example. Also included are the use of further oxidation agents such as carbon dioxide or metal oxides and the overall management of oxygen levels. Implied in this oxygen management is the accumulation or concentration of metal oxide impurities along with noble metals providing dross of significant economic potential.
- 1.06 Thermal Decomposition is to include heating of the feedstock to separate volatile materials as well as any process or apparatus used for or in conjunction to this purpose. In accordance with best modes of operation it is assumed that this subsystem is coupled to the Steam 30 Methane Reaction (1.05) and Chlorination (1.09) subsystems which provide hot gases utilized by this subsystem to volatilize the feedstock, in turn cooling and reacting the gases before processing by Hydrotreatment (1.15). Feedstock may be fed directly to this subsystem 35 or as intermediate streams from other subsystems. Regardless of the specific arrangement of this subsystem, it serves to convert fed materials to gases and char residue consisting of inert mineral, spent catalyst, and fixed carbon which are then processed by Chlorina- 40 tion (1.09). This is in contrast to conventional staged reforming involving direct oxidation and/or heat reclamation.
- 1.07 Hot Solids Recycle is to include processes reclaiming heat from the remaining solid oxides exiting Chlorination (1.09). In accordance with best modes it is assumed that this useful heat is to be transferred to water/steam and that recovery of salts from brine is to be included as well. These salts are then utilized in Gas Cleanup and Processing (1.10) through the formation of carbonate 50 minerals. Oxides having their useful heat recycled may be discharged as tailings or used within construction or other industries.
- 1.08 Electrochemical Processing is to include a wide range of processing methods available to advantageously drive 55 redox reactions through electrochemical means. This includes molten salt or gaseous electrolysis through solid or liquid electrolytes/electrodes as well as plasma processing. This subsystem is assumed to be operating between or in tandem with the Steam Methane Reaction (1.05) and Chlorination (1.09) subsystems and further includes the circulation of molten lead between the two. In accordance with best modes it is envisioned such lead circulation may be carried out by magneto-hydro-dynamic pumping, conventional pumping, or gravity and 65 displacement. Within this subsystem, substantially all metals that are not to be discharged to Hot Solids

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Recycle (1.07) are extracted from the Chlorination (1.09) output. There may be methods employed for this purpose that are equivalent, better than, or supplementary to electrochemical processes that for the purposes of this disclosure fall within this subsystem. Although conventionally direct current is utilized in similar apparatus, the present invention is not preferential to alternating or direct current within this subsystem.

- 1.09 Chlorination is to include any method or apparatus utilized for the purpose of indirect oxidation of the carbon constituent of the char produced by Thermal Decomposition (1.06) subsystems and chlorination of intermixed metals. This is in contrast to oxidation methods typical of staged reforming or gasification in that metal chlorides are produced. In accordance with a best mode of carrying out the present invention embodiments such as a rotating kiln, fluidized bed, manifold fluidized bed, or partially fluidized bed seem most suitable. A plurality of chlorides can be allowed to volatilize from the chlorinator then separated from the carbon oxides produced or alternatively kept within a chloride melt and electrodeposited. The present invention is not preferential to either processing technique. Volatilized chlorides not captured for removal will migrate to the Thermal Decomposition (1.06) subsystem, reacting with present oxides, and drop out or are filtered from the gas stream. Hot carbon monoxide from the Electric Arc Processing (1.12) or a similar process is also utilized as an oxygen sink. Further, carbon dioxide or various metal oxides and chlorides may be introduced to moderate reactivity and temperature. Dependent on the embodiment, thermal management is a major consideration for optimal operation as the heat generated drives the Thermal Decomposition (1.06) and Steam Methane Reaction (1.05) subsystems through transfer of materials. Electrochemical Processing (1.09) is one method available to maintain high operating temperatures with various complementary benefits.
- 1.10 Gas Cleanup and Processing is to include primarily the management of sulfur and carbon dioxide which may include conventional management processes such as acid gas stripping, chlorine knockout, dust collection, ammonia collection, cryogenic separation, sulfuric acid or Claus processes. Depending on the embodiment, sulfur dioxide from the Flash Smelting (1.04) and hydrogen sulfide from the Condensation\Distillation (1.13) may be reacted directly in a Claus process replacing or relieving the need for air or oxygen feed. Capture of either gas with calcium carbonate is also commonly practiced. In accordance with best modes this subsystem further utilizes alkali and alkaline chlorides from the Hot Solids Recycle (1.07) subsystem in a modified Solvay process for the capture of carbon dioxide as carbonate minerals. Within this disclosure the use of the term alkali chloride(s) or alkaline chloride(s) are considered to be synonymous and include Group 1 and Group 2 elements due to similar processing reactions. Due to this distinction, various methods of chlor-alkali, lime, and fertilizer production may directly relate to this subsystem, although Fertilizer Production (1.17) has its own subsystem maximal separation both in classification and physical proximity of these subsystems is considered in the best mode of carrying out the present invention. Cleanup is performed on the uncondensed gases from the Condensation/Distillation (1.12) subsystem and involves removing hydrogen chloride, hydrogen sulfide, and ammonia produced in the Hydrotreatment (1.15)

from the gas. Carbon dioxide that is not mineralized may be recycled by conventional synthesis gas processing techniques operating within this subsystem or reprocessed within the superstructure of the invention by passing it through. Furthermore this subsystem may be expanded to include the entire range of applicable petrochemical processes in which case the synthesis gas processing involved has significant complementary overlap with Petrochemical Production (1.16) subsystems.

- 1.11 Coal Coking is to include means of contacting preheated coal from the High Temperature Coal Hopper (1.14) with hot gases from the Electric Arc Processing (1.12) volatilizing and cracking entrained hydrocarbons and producing a coke product. Volatilized gases are then 15 sent to the Thermal Decomposition (1.06) subsystem while coke and/or reduced metals present may be introduced to the Electric Arc Processing (1.12) or other applicable processes.
- 1.12 Electric Arc Processing is to include any configuration 20 of electric arc furnace apparatus that may further benefit the integrated processes through: recycling of steels, production of steel from direct reduced or electro won iron, acting as a high temperature carbon monoxide source, an appropriate carbon sink for coke, a high tem- 25 perature apparatus for heating and reacting metals, slags, or gases from other processes, formation of slag appropriate as a heat carrier to other processes, reduction of silica or alumina to their metallic forms, production of metal chlorides for the chlorinator, or for leaching 30 noble metals from molten metal to a lead alloy suitable for introduction to the Steam Methane Reaction (1.05). In accordance with best modes, a major advantage to incorporating this subsystem would be utilizing electricity produced through Supplemental Heating (1.02) to 35 provide high temperature gases to the Chlorination (1.09) and Coal Coking (1.11) subsystems.
- 1.13 Condensation/Distillation is to include means for separating a fraction or fractions of the gas stream from the Hydrotreatment (1.15) producing a crude oil or varying fractions thereof for the Petrochemical Production (1.16) subsystem. Uncondensed gases flow through to Gas Cleanup and Processing (1.10).
- 1.14 High Temperature Coal Hopper is to include means for preheating coal to be sent to the Coal Coking (1.11) 45 subsystem by contact with hot gases from Hydrotreatment (1.15). Further, this direct contact may be used to partially volatilize the coal producing a near-coke. Methods of condensing a portion of the high molecular weight fraction of the gas stream and passing it to the Coal Coking (1.11) for cracking may also be utilized. Utilizing sulfur sorbent mixed with the coal as well as circulation or fluidization between this subsystem and the Hydrotreatment (1.15) and Coal Coking (1.11) subsystems are considered best practices. Management of 55 vaporous mercury present in the gas feed could also be carried out in this manner.
- 1.15 Hydrotreatment is to include the processing of volatilized gases from the Thermal Decomposition (1.06) with large amounts of hydrogen generated by the Steam Methane Reaction (1.05) through a high pressure moderate temperature reactor. It may further include the utilization of conventional catalysts as well as alkali\alkaline catalysts which react to form carbonates and drive the water gas shift reaction. The overall object of the subsystem is to saturate the hydrocarbon gases, simultaneously reacting to form hydrogen sulfide,

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- hydrogen chloride, and ammonia which can then be removed in the Gas Cleanup and Processing (1.10) subsystem. Destruction of a plurality of organic pollutants is further achieved within this subsystem.
- 1.16 Petrochemical Production is to include the processing and handling of bulk or fractionated hydrocarbons from the Condensation/Distillation (1.13) as well as light gases from Gas Cleanup and Processing (1.10) and is meant to cover the entire range of petrochemical processing. Also included are blending, refining, and preparation for transport such as by pipeline or rail.
- 1.17 Fertilizer Production is to include the integration of ammonia production through reaction of hydrogen supplied by Hydrogen Separation (1.01) and nitrogen supplied by other subsystems such as the Flash Smelting (1.04) after passing through Gas Cleanup and Processing (1.10). Further it is to include the production of ammonium or alkali/alkaline salts such as carbonates, phosphates, nitrates, sulfates, sulfides, or urea.

In one embodiment of the present invention, tar sand production may be of primary importance. Utilizing the Core and Recommended subsystems of FIG. 1, along with Petrochemical Processing (1.16) a light sweet synthetic crude oil for pipeline transportation is produced with zero harmful emissions, wastewater, or hazardous tailings and complete carbon conversion conserves more chemical energy of the feedstock than conventional processing. Sand and carbonates may be utilized along with steam produced for further in-situ tar sand recovery. Furthermore, biomass and poly-metallic shale can be fed into the system taking advantage of both the carbon conversion efficiency and metal separation.

Another embodiment of the present invention is beneficial where mixed sulfide ores may be within an economically reasonable distance of mineable shale and coal formations. Utilizing the Core and Recommended subsystems of FIG. 1, along with the Flash Smelting (1.04), Coal Coking (1.11), Electric Arc Processing (1.12), and High Temperature Coal Hopper (1.14) a plurality of metals can be extracted with a lower environmental footprint than conventional operations.

In a further embodiment of the present invention, municipal water treatment and solid waste management are integrated with district heating and electricity generation. Utilizing the Core and Recommended subsystems of FIG. 1, Fertilizer Production (1.17) could be further integrated to ensure valuable nutrients are recycled. Fischer-Tropsch processing within the Gas Cleanup and Processing (1.10) subsystem can further be used to provide automotive fuels.

In a final embodiment of the present invention, all of the Core, Recommended, and Optional subsystems of FIG. 1 are utilized in a large scale combined cycle poly-generation plant providing electricity, heating, cooling, and fresh water to a large metropolitan area. Capitalizing on economies of scale, such a superstructure could operate on advantageous feed-in tariffs for the disposal of a variety of wastes over a wide geographical area. It would further be capable of integrating distributed generation into its regional power grid through a plurality of operational modes, operating high energy demand subsystems during off-peak hours while lowering chemical output and instead utilizing that chemical energy during periods of high demand.

INDUSTRIAL APPLICABILITY

alkali\alkaline catalysts which react to form carbonates and drive the water gas shift reaction. The overall object of the subsystem is to saturate the hydrocarbon gases, simultaneously reacting to form hydrogen sulfide,

tion finds industrial applicability in the pollution management and environmental footprint context of a wide range of industrial processing methods.

SCOPE OF THE INVENTION

Having illustrated and described the principles of the system and method of the present invention in various embodiments, it should be apparent to those skilled in the art that the embodiment can be modified in arrangement and detail with- 10 out departing from such principles. For example, the carbonaceous feedstock may be entirely consumed on site if preferred. Therefore, the illustrated embodiments should be considered only as example of the invention and not as a limitation on its scope. Although the description above con- 15 tains much specificity, these should not be construed as limiting the scope of the invention but as merely providing illustrations of some of the presently preferred embodiments of this invention. Further, it is appreciated that the scope of the present invention encompasses other embodiments which 20 may become obvious to those skilled in the art, and that the scope of the present invention is accordingly to be limited by nothing other than the appended claims, in which reference to an element in the singular is not intended to mean "one and only one" unless explicitly so stated, but rather "one or more". 25 All structural and functional equivalents to the elements of the above-described preferred embodiment that are known to those of ordinary skill in the art are expressly incorporated herein by reference and are intended to be encompassed by the present claims. Moreover, it is not necessary for a device 30 or method to address each and every problem sought to be solved by the present invention for it to be encompassed by the present claims.

The invention claimed is:

- 1. A method for the integration of carbochlorination into a 35 staged reforming operation, the method comprising:
 - step i. delivering a feedstock to a thermal decomposition stage where the feedstock is reacted with a gas and volatized through a plurality of thermochemical steps to yield a gas stream and a solid residue comprising a spent 40 catalyst, an inert mineral, and a formed coke;
 - step ii. chlorinating the solid residue in a carbochlorination process to produce a gas comprising carbon oxides and a multi-phase residue comprising a molten or semi-molten salt, metal, or metal compound;
 - step iii. reacting water and a portion of the gas stream of step i. in a hydrogen production process to produce a carbon gas comprising hydrogen, wherein at least a portion of the multi-phase residue is used as a heat carrier between the carbochlorination process and the hydrogen 50 production process;
 - step iv. delivering at least a portion of the gas produced in step ii. or step iii. to the thermal decomposition stage of step i. to be used as the gas reacted with the feedback; and
 - step v. delivering at least a portion of the gas stream formed in step i. to a downstream process.
 - 2. The method of claim 1, wherein
 - a portion of the gas containing carbon oxides is mineralized.
- 3. The method of claim 1, wherein the downstream process includes:
 - petrochemical production, hydrocarbon refining, bio-refining, metal refining, rare earth separation, ceramics fabrication, glass production, fertilizer production, 65 potable water production, desalination, water treatment, landfill reclamation, environmental remediation, soda

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- ash production, chlor-alkali processing, or hazardous or radioactive materials processing.
- 4. The method of claim 1, wherein the multi-phase residue used as a heat carrier also functions as a catalyst.
- 5. The method of claim 1, wherein the molten metal comprises lead.
- 6. The method of claim 1, wherein the molten metal comprises a lead alloy, further comprising the step of delivering the lead alloy to an oxidizing vessel and oxidizing the lead alloy.
- 7. The method of claim 1, wherein the carbochlorination process is operated at between 700 to 1300 degrees centigrade.
- 8. The method of claim 1, wherein the multi-phase residue includes silica, further comprising transferring a sensible heat of the silica to steam in a hot solids recycle process.
- 9. The method of claim 8, wherein the multi-phase residue includes other metal oxides.
- 10. The method of claim 1, wherein the carbochlorination process produces a metal chloride melt and volatile metal chlorides and oxychlorides.
- 11. The method of claim 10, further comprising electrolyzing the metal chloride melt.
- 12. The method of claim 10, further comprising reacting the metal chloride melt with ammonia, water, and carbon dioxide to form ammonium chloride and alkali carbonates to mineralize the gas containing carbon oxides.
- 13. The method of claim 10, wherein the metal chloride melt includes chlorinated rare earth elements.
- 14. The method of claim 10, wherein the metal chloride melt includes chlorinated radioactive materials.
- 15. The method of claim 1, further comprising fluxing the carbochlorination process with a supplemental molten lead feed in which lead is reacted with a chlorination agent forming lead(ii)chloride that in turn reacts with alkaline oxides in a chlorinator to produce alkaline chlorides and litharge then further reacting with carbon to form a metallic lead.
- 16. The method of claim 1, wherein the carbochlorination process is supplemented by an electrochemical processing that utilizes at least two electrodes comprising an anode and cathode system with one or more electrodes and/or electrolytes formed by lead and/or lead compounds.
- 17. The method of claim 16, wherein the electrochemical processing removes oxygen.
 - **18**. The method of claim **16**, wherein the electrochemical processing includes utilizing a plasma forming apparatus.
 - 19. The method of claim 1, wherein the hydrogen production process utilizes a steam methane reactor operated at between 500 to 1100 degrees centigrade.
 - 20. The method of claim 1, wherein the hydrogen production process utilizes a steam methane reactor and the multiphase residue used as the heat carrier includes lead, and wherein metal impurities in the lead are separated.
 - 21. The method of claim 1, wherein the thermal decomposition stage includes the addition of materials recycled from an attached process.
 - 22. The method of claim 1, wherein the thermal decomposition stage utilizes and a mixed flow-through catalyst.
 - 23. The method of claim 22, wherein the feedstock is heated and reacted to obtain a char residue consisting essentially of an unreacted feedstock, a spent catalyst, and a coked carbon, further comprising passing the char residue through a counter-current heat exchanger in direct contact with a gas and passing the char residue into a chlorination reactor and forming a gas including carbon dioxide, a molten chloride salt, an inert solid residue, and a molten metal alloy.

- **24**. The method of claim **22**, wherein the thermal decomposition stage further comprises treating the product gas with hydrogen in a hydrotreatment vessel.
- 25. The method of claim 1, further comprising passing the product gas through a bed of coal to heat the coal, simultaneously cooling and condensing a portion of the product gas and removing a condensed hydrocarbon and a mercury compound from the product gas.
- **26.** The method of claim **25**, further comprising passing the coal the mercury compound, and condensed hydrocarbon into a reactor and cracking and volatizing the condensed hydrocarbon.
- 27. The method of claim 26, wherein the formed coke is utilized as a heat carrier or a reactant in a process.
- 28. The method of claim 1, wherein the product gas is condensed by a pressure condenser or flash drum to obtain a light sweet crude oil being nearly free of contaminates comprising one or more of the following: mercury, sulfur, oxygen, nitrogen, halides, heavy metals, and organic pollutants.
- 29. The method of claim 1, wherein the gas streams within the process may be stripped of hydrogen by means of pressure swing adsorption, molecular sieves, or proton conducting ceramics.
- **30**. The method of claim **1**, further comprising utilizing one ²⁵ or more of the following:
 - i. a heat source
 - ii. a feedstock preparation stage
 - iii. a converter for the primary or secondary flash smelting of mineral sulfides or sulfates including lead, copper, zinc, nickel, tin, bismuth, and antimony sulfides

iv. an electric arc furnace.

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- **31**. The method of claim **30**, wherein the heat source is a modular nuclear reactor, a geothermal, concentrated solar, or hydrocarbon fired boiler.
- 32. The method of claim 30, wherein the feedstock preparation stage includes producing a blended feedstock.
- 33. The method of claim 30, wherein the feedstock preparation stage produces a crushed, shredded, blended, powder, pulp, fluid, or fluidizable composition.
- 34. The method of claim 33, wherein the feedstock composition is a coal based blend consisting substantially of any grade coal optionally enriched with oxides of iron, silicon, aluminum or any other minerals typically found in iron ore or its concentrates following a beneficiation process.
- 35. The method of claim 33, wherein the feedstock is a mixed hydrocarbon feedstock consisting essentially of hydrogen rich heavy oils or tars blended with a carbonaceous material and catalytic agent.
- 36. The method of claim 35, wherein the carbonaceous material comprises one or more of the following: extra heavy crude, heavy crude, bitumen, oil sands, kerogen, oil shale,
 biomass, sewage sludge, landfill waste, contaminated soil, black liquor, tires, asphalt, plastics, rubbers, and agriculture residues.
 - 37. The method of claim 35, wherein the catalytic agent comprises one or more of the following: red mud, phosphogypsum, and alkali salts.
 - **38**. The method of claim **30**, wherein the converter produces a slag appropriate for sending to the thermal decomposition stage as a heat carrier as well as a source of metals.
 - **39**. The method of claim **30**, wherein the converter produces a lead bullion for sending to the hydrogen production process.

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